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New Aspects in the Coordination Chemistry of Ge- and Sn-Containing Metallaaromatic Compounds

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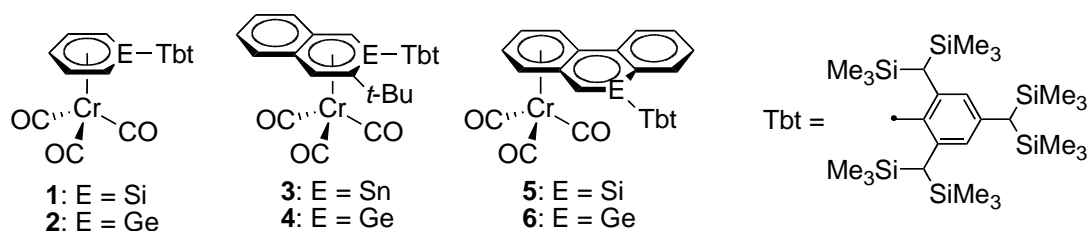
Running Head: Coordination Chemistry of Metallaaromatic Compounds

Abstract: Ge- and Sn-containing η^6 -Metallaarene–Cr(CO)₃ complexes showed unique reactivity leading to the formation of unexpected products. The formation mechanism of the new complexes was discussed together with their molecular structures.

Keywords: metallaaromatic compound, chromium, coordination chemistry

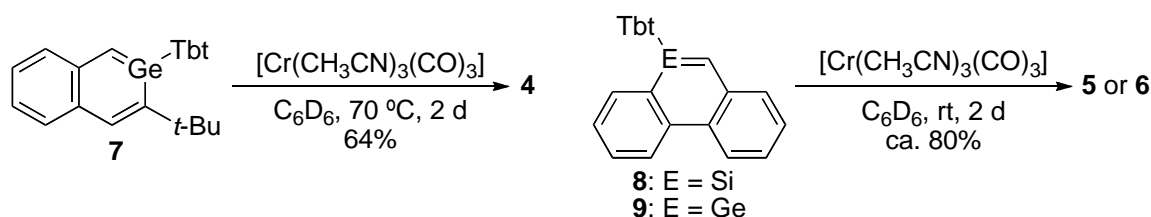
Introduction: We have already succeeded in the synthesis and isolation of various stable metallaaromatic compounds containing a heavier group 14 element (*heavy aromatics*) by taking advantage of kinetic stabilization afforded by an efficient steric protection group, Tbt [1]. As an extension of this chemistry, we have examined the complexation of sila- and germabenzenes and 2-stannanaphthalene by the ligand exchange reactions with

$[M(\text{CH}_3\text{CN})_3(\text{CO})_3]$ ($M = \text{Cr}, \text{Mo}, \text{W}$) and succeeded in the isolation of the corresponding η^6 -metallaarene complexes **1–3** [2]. Here, we present the synthesis of novel η^6 -metallaarene- $\text{Cr}(\text{CO})_3$ complexes containing a Si or Ge atom in the metallaaromatic ring (**4–6**) together with the unique reactivity of **3–6** leading to the formation of unexpected products.



Results and Discussion: Ligand exchange reactions of isolated 2-germanaphthalene **7** and 9-metallaphenanthrenes **8** and **9** were performed according to the procedures similar to those previously reported for the complexes **1–3** (Scheme 1).

Scheme 1.

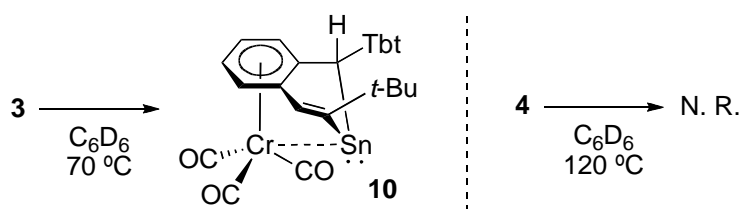


In the case of **7**, the coordination of $\text{Cr}(\text{CO})_3$ moiety occurred at the GeC_5 ring similarly to 2-stannaphthalene **3**. In the cases of **8** and **9**, on the other hand, $\text{Cr}(\text{CO})_3$ moiety coordinated to the C_6 -ring far from Tbt group instead of to the EC_5 rings, complexes **5** and **6** keep isolated metallene ($\text{Si}=\text{C}$, $\text{Ge}=\text{C}$) moieties. The ^1H NMR signals of 10-position were observed at 6.33 (**5**) and 7.17 (**6**) ppm, which values are dramatically high-field shifted from those of **8** and **9**

(**8**: 7.27; **9**: 8.13 ppm). These results indicated the increase of double-bond character of metallene moieties and the decrease of π -electron delocalization on the central EC₅ rings.

Although complex **4** has high thermal stability, heating of tin-analogue **3** at 70 °C afforded unusual stannylene complex **10** quantitatively, in which Tbt group migrated to the neighboring carbon of the tin atom and the Cr(CO)₃ moiety moved to the C₆-ring (Scheme 2).

Scheme 2.

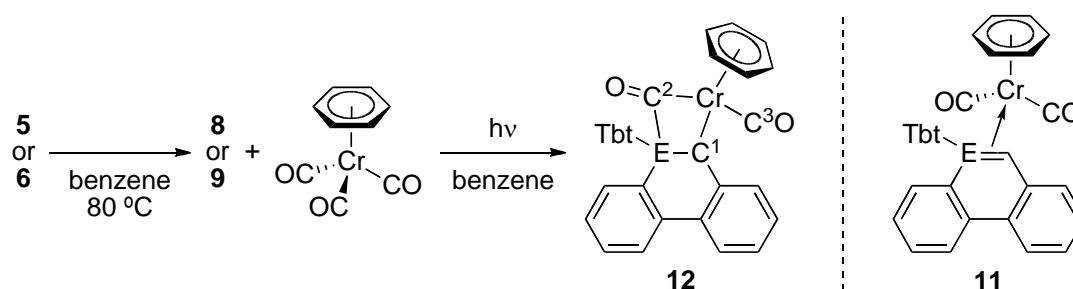


This reactivity is characteristic of the stannanaphthalene–Cr(CO)₃ complex, and the free 2-stannanaphthalene is stable under the same conditions. In the ¹¹⁹Sn NMR of **10**, the signal appeared at –573 ppm, which is an unusual value as that of a stannylene (typically around ca. +2000 ppm), indicating some interaction between the Sn and Cr atoms. Actually, the X-ray crystallographic analysis of **10** revealed the close Sn...Cr distance [3.1214(8) Å], which is much shorter than the sum of van der Waals radii of Sn and Cr atoms (4.17 Å).

Complexes **5** and **6** were thermally stable at room temperature in the solid state. However, heating of the benzene solution of **5** or **6** at 80 °C resulted in the ligand exchange to afford the mixture of free **8** or **9** and [(η⁶-benzene)Cr(CO)₃] (Scheme 3). Unexpectedly, on standing at room temperature, these mixtures were found to give the corresponding new complexes slowly. This reaction was assisted by photo-irradiation and completed after 13 hours (Scheme

2). Judging from the results of the ^1H and ^{13}C NMR spectroscopy, the structures of the products were initially assigned as π -complexes **11**, which might be generated by the leaving of one CO ligand by photo-irradiation and the coordination of the metallene moiety to the vacant coordination site of the chromium center. However, X-ray crystallographic analyses of the products clearly showed the evident interaction between the Si or Ge atom and the carbon atom of CO, which may be rationalized with the novel four-membered metallacycles postulated as **12**. The distances of $\text{E}-\text{C}^2$ were found to be 2.374/2.286 (Si) and 2.475/2.498 (Ge) Å, respectively, which are longer than the typical lengths of E–C single bonds [1.88 (Si) and 1.95 (Ge) Å] and much shorter than the sums of the van der Waals radii [3.80 (Si+C) and 3.70 (Ge+C) Å]. These significant interactions were supported by the two distinguishable signals of CO in their ^{13}C NMR spectra.

Scheme 3.



Conclusions: We have succeeded in the synthesis of novel types of $\text{Cr}(\text{CO})_3$ complexes of metallaaromatic compounds **4–6**. Of particular notes among the unique reactivity of the new complexes are the thermolysis of **3** and the photolysis of **5** and **6** leading to the formation of

unprecedented types of complex **10** and **12**. Detailed investigation of the structures of newly obtained complexes from experimental and theoretical aspects and further elucidation of the reactivity of complexes **3–6** will be reported elsewhere.

References:

- [1] For a review, see: Tokitoh, N. *Acc. Chem. Res.* 2004, 37, 86.
- [2] a) Shinohara, A.; Takeda, N.; Sasamori, T.; Matsumoto, T.; Tokitoh, N. *Organometallics* 2005, 24, 6141. b) Nakata, N.; Takeda, N.; Tokitoh, N. *Angew. Chem. Int. Ed.* 2003, 42, 115. c) Mizuhata, Y.; Sasamori, T.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc.* 2006, 128, 1050. d) Mizuhata, Y.; Sasamori, T.; Nagahora, N.; Watanabe, Y.; Furukawa, Y.; Tokitoh, N. *Dalton Trans.* 2008, 4409.